

## FEASIBILITY STUDY OF spICP-MS FOR THE DETERMINATION OF THE STRUCTURE AND COMPOSITION OF BIMETALLIC NANOPARTICLES

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### Abstract

Our present work is focused on the spICP-MS measurement of bimetallic (gold-silver core-shell and alloy) nanoparticles. We found that suitable measurement conditions and data evaluation approaches actually allow the determination of not only the elemental composition (Au:Ag molar ratio) of such particles, but we can gain information about their structure too. Our paper will present data obtained by using both regular (millisecond-range) and high (microsecond-range) time resolution spICP-MS experiments.

### Introduction

Nanoscience is a rapidly developing field in science and technology. Nanomaterials (nanoparticles, nanocomposites, nanostructures, etc.) are nowadays widely used in a broad range of application fields including medicine, catalysis, energetics, sensorics, etc. Certain bimetallic nanoparticles (BNPs) have tunable magnetic, catalytic and optical properties, therefore they have been designed and synthesized in great numbers for novel application areas in recent years. The morphological and compositional characterization of zero dimensional nanocomposites or BNPs are traditionally done by a combination of methods including electron microscopy (TEM, SEM-EDS), X-ray diffraction (XRD), UV-Vis spectroscopy, X-ray photoelectron spectroscopy (XPS), or atomic spectroscopy following dissolution [1].

Single particle, or particle-mode, inductively coupled plasma mass spectrometry (spICP-MS) is a novel technique where ICP-MS spectrometers are used in the time-resolved mode for the measurement of dilute nanodispersions. Each detected NP produces a narrow signal peak (a few hundred  $\mu$ s in duration) with a height (count) that is proportional to the mass of the analyte in the NP. The dwell time (or integration time) is typically in the 5-10 ms range in order to minimize the occurrence of NP signal peak overlaps. After the statistical evaluation of the signal time profile, information can be obtained about not only the elemental (isotopic) composition of the NPs, but also their size distribution, as well as the particle concentration. The measurement is fast (takes only a couple of minutes) and the required sample volume is also small (a few mL). For monometallic NPs, typical size detection limits range from 10 to 30 nm [2].

Recently, quadrupole ICP-MS instruments with 100 microsecond or less dwell times („high resolution”) became available commercially (e.g. Perkin Elmer NexION). The introduction of high resolution spICP-MS (HR-spICP-MS) provides new possibilities and advantages, such as offering dual-element detection capability, lowered spectral backgrounds and resolution of particle peak profiles, but it also seems to generate new drawbacks, e.g. increased split-particle events and decreased sensitivity [3]. In this study, the information that can be obtained by combining normal and high resolution single particle ICP-MS (spICP-MS) measurements for spherical bimetallic nanoparticles (BNPs) was assessed.

### **Experimental**

Two ICP-MS instruments were used in the experiments. Normal resolution spICP-MS (dwell time was set to 6 ms) and solution-mode ICP-MS measurements were performed on an Agilent 7700x type instrument, while HR-spICP-MS measurements (dwell time was set to 20  $\mu$ s) were carried out on a Perkin Elmer NexION 350 instrument. NP data was always collected in the time-resolved analysis (TRA) mode. On the NexION 350, the Syngistix Nano Application Module was used. Pre-processing of the collected data was necessary prior to the statistical evaluation of HR-spICP-MS measurements. For this purpose, we developed and used a macro-based program, written in Visual Basic for Applications (Microsoft, USA). This program counted individual particle events in the dataset and calculated the transit time of their ion cloud. Particle discrimination was based on the condition that a particle peak should be preceded and followed by at least three datapoints with zero signal. The transit time was then calculated as the product of the number of data points in that event and the dwell time. The total particle signal for a given NP detection event was obtained as the sum of time-resolved signals in that event.

A series of standard PELCO NanoXact nano-dispersions containing tannic acid capped gold and silver NPs obtained from Ted Pella (Redding, California, USA) were used for spICP-MS size calibration. The certified size of the gold NPs used were 28.8, 39.3, 61.3 and 75.4 nm, whereas the diameter of the silver NPs were 43.4, 59.0, 82.1 and 95.7 nm. Sodium citrate stabilized, silver-shelled gold nanospheres with 79.0 nm diameter (51.0 nm core diameter and 14.0 nm shell thickness) were obtained from NanoComposix (San Diego, USA). Gold-silver alloy nanoparticles - with 40:60, 60:40 and 80:20 molar ratios – have been synthesized with the combination of co-reduction of gold and silver salts and seeded growth methodology [4].

For sample preparation purposes of solution-mode ICP-MS measurements ultratrace quality HCl and HNO<sub>3</sub> acids (VWR Chemicals, Pennsylvania, USA) were used. The duration of dissolution of the composite NPs, which was carried out by heating the sample at 170 °C in aqua regia, was one hour. Calibration in solution-mode was performed using the Agilent Multi-Element Calibration Standard-3 (for gold) and Inorganic Ventures IV-ICPMS-71A (for silver).

### **Results and discussion**

The single particle ICP-MS (Method A) has the potential to become a practical alternative technique for the determination of the concentration of the component elements in composite NPs. Therefore, we carried out comparative measurements to assess its accuracy and precision in the case of Au-Ag alloy BNPs. We tested the performance of spICP-MS with normal time resolution (6 ms) against two solution-mode ICP-MS approaches: i) direct NP nebulization (Method B) and ii) conversion of the nanodispersion to a real solution by acid digestion of the NPs (Method C). As can be seen in **Table 1.**, there is a good agreement between the nominal

molar ratio and the results of solution mode ICP-MS after acidic digestion and spICP-MS. The advantage of spICP-MS is that the measurements are largely free from the influence of dissolved contaminants in the nanodispersion and the analysis is fast, as sample preparation is reduced to a simple dilution. At the same time, results of solution mode ICP-MS with direct NP nebulization can not be considered as accurate. The precision (RSD%) value is also poorer in the latter case.

Particle	Method A			Method B		Method C	
	Nominal Au/Ag molar ratio	Found Au/Ag molar ratio	Precision	Found Au/Ag molar ratio	Precision	Found Au/Ag molar ratio	Precision
Au-Ag core-shell	0.7500	0.6895	0.0058	0.3579	0.0269	0.7234	0.0211
Au-Ag alloy (40:60)	0.6667	0.7444	0.0111	1.639	0.0880	0.7560	0.0254
Au-Ag alloy (60:40)	1.500	1.585	0.0358	3.207	0.1988	1.586	0.0531
Au-Ag alloy (80:20)	4.000	3.934	0.0838	10.11	0.7976	4.320	0.1650

Table 1. A comparison of the analytical performance of three approaches used for the determination of the composition of Au-Ag bimetallic NPs.

Method A: spICP-MS analysis; Method B: Solution-mode ICP-MS analysis with direct particle nebulization; Method C: Solution-mode ICP-MS analysis after particle dissolution.

As a step towards the investigation of the structure of spherical BNPs, we studied the high resolution signal time profile for monoelemental gold and silver spherical nanoparticles, with the central interest of the transit time of the ion cloud through the instrument and the shape of the signal time profile.

We found that the transit time of the ion cloud correlates fairly linearly with the particle diameter (Figure 1.), as it can be more or less expected. A further observation can also be made, namely that the transit time for the same particle diameter is longer for gold than for silver.

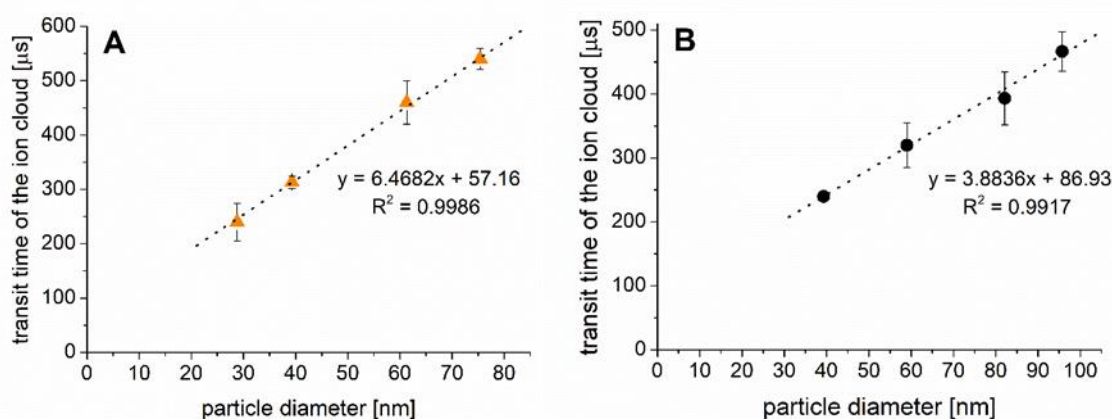


Figure 1. Correlation of transit time with the diameter for gold (A) and silver (B) spherical nanoparticles. Error bars indicate standard deviation from three repeated measurements

In order to obtain reliable, characteristic data about the structure of the investigated BNPs, we

applied filtering according to the total NP signal (the integrated signal for one NP detection event in the HR-spICP-MS) and the transit time. This was executed by only retaining those time profiles from the collected dataset which produced a total NP signal equal to, within a  $\pm 10\%$  tolerance range, the mode (maximum) of the lognormal function fitted to the signal histogram, and the same transit time within a  $\pm 10\%$  tolerance range. As an example, **Figure 2.** shows the average signal time profile for an 80 nm Ag NP. The shape of the profile is fairly Gaussian. The presented signal profile was calculated by averaging, after executing the filtering.

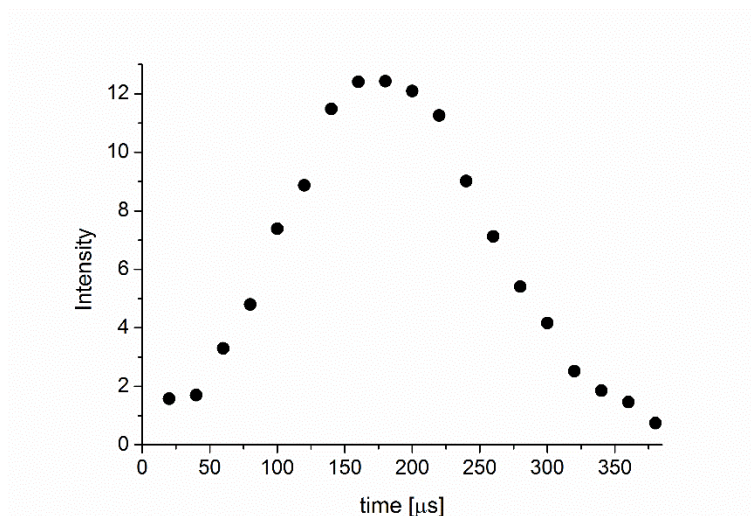


Figure 2. Average signal time profile for an 80 nm nominal diameter spherical Ag nanoparticle.

Applying the data evaluation method presented above we can obtain beneficial information about the structure of BNPs. Component elements in homogeneous alloy particles results in signal profiles that have comparable shape and duration, whereas, it is distinctly different for the ion cloud of the core and the shell of a core-shell BNP. Detailed experimental data on this matter will be disseminated in our presentation.

## References

- [1] A. Sápi, A. Kéri, I. Kálomista, D.G. Dobó, Á. Szamosvölgyi, K.L. Juhász, Á. Kukovecz, Z. Kónya, G. Galbács, *Anal. At. Spectrom.* 32 (2017) 996.
- [2] S. Lee, X. Bi, R.B. Reed, J.F. Ranville, P. Herckes, P. Westerhoff, *Environ. Sci. Technol.* 48 (2014) 10291.
- [3] M.T. Montano, H.R. Badiei, S. Bazargan, J.F. Ranville, *Environ. Sci.: Nano* 1 338 (2014) 338.
- [4] D. Rioux, M. Meunier, *J. Phys. Chem. C* 119 (2015) 13160.